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[17] **29**: $[\alpha]_D^{23} = +44.5$ ($c = 0.09$ in MeOH).

Intermolecular Hydrogen Bonding between Water and Pyrazine**

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Hydrogen bonds involving aromatic rings, especially those containing heterocyclic nitrogen atoms, are of fundamental importance in nature. For example, they are essential in base pairing of oligonucleotides, and they determine the tertiary structure and functions of biopolymers. Since all these processes occur in an aqueous environment, the corresponding interactions with water are also of particular interest.[1]

Although it had been speculated for many years that the π-electron cloud of aromatic rings could act as a hydrogen-bond acceptor, the position of hydrogen was first established unambiguously through rotational spectra from the 1:1 complex of benzene with water obtained in a supersonic expansion.[2, 3] Thus, it has been shown that the water molecule is located above the plane of the benzene ring, subject to nearly free internal rotation, with both hydrogen atoms pointing toward the π cloud.

Because aromatic nitrogen heterocycles are essential components of proteins and nucleotides, we thought it would be interesting to study the nature of the interactions of such compounds with water. Rotational transitions of pyridine/water have already been described, but that research project has since been abandoned.[4] Although pyrimidine is the most common six-membered aromatic ring in nature, we chose pyrazine (PRZ) as a prototype, because in this case only the spectrum of the complex is observable in the aromatic-ring/water mixture, since PRZ itself produces no rotational spectrum (the electric dipole moment μ is zero due to symmetry).

Evidence of hydrogen-bond formation between PRZ and water has been obtained from electronic spectra recorded in solution[5] and in an argon matrix,[6] but extensive efforts to observe the formation of such complexes in a supersonic expansion were unsuccessful.[7] The position of the hydrogen atom has not been precisely determined; nevertheless, the blue shift of the $n-\pi^*$ transition strongly suggests that the hydrogen atom is bound to the nitrogen atom. The effects of hydrogen bonding interactions on the electronic molecular spectra of PRZ/water complex and PRZ in solution have been investigated theoretically by Zeng et al.[8] In all cases the interpretations of experimental spectra rely on the assumption of a linear structure for the $OH\cdots N$ bond.

Molecular beam Fourier transform microwave (MBFTMW) spectrometers have frequently been used for the investigation of rotational spectra of molecular complexes of aromatic

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molecules. Reported spectra include those of six-membered aromatic rings, either with rare gases[9–16] or with small polar molecules. [2, 3, 17] Since we were recently successful in investigating molecular complexes of six-membered aromatic molecules with a simpler technique[18–20]—supersonic jet millimeter-wave absorption spectroscopy—we decided to apply this technique to complexes of aromatic molecules with water as well.

PRZ has two types of proton-acceptor sites: the ring π cloud and the nitrogen lone pair; rotational constants of the complex have therefore been estimated according to two models: the water molecule is bound a) above the ring and subject to the same intermolecular distances as in the benzene/water complex, and b) in the plane of the ring, with a linear N ··· H–O arrangement and an N–H(O) bond length of 1.9 Å.[7] The geometry of PRZ was taken from the literature[21] under the assumption that it remains unaltered in the complex. From the derived rotational constants, and based on symmetry considerations, the following rotational spectra might have been expected: a μ_a-type spectrum in case a) and both μ_a- and μ_b-type spectra in case b) (μ_a and μ_b are dipole moments along the *a* and *b* axes).

In accordance with model b), the experimental spectrum showed several lines of type μ_b in the R branch, with high values for the quantum number *J* (overall angular momentum) and K_a (the component about the *a* axis for a prolate rotor). The latter is composed of two overlapping components as a result of quasi-degeneracy of the associated levels. All the observed transitions were split into two components, with a relative intensity of 5:3 or 3:5 depending on the parity of K_a. The intensity ratios alternate for consecutive k_a values. After assignment of the rotational spectrum of the complex with normal water, spectra of the isotopomers with D_2O, HDO, and $H_2{}^{18}O$ were investigated. The same types of spectra were observed for all four isotopomers with respect to the doubling of lines and the intensity ratios. It is interesting to note that in the case of the PRZ/HDO complex two isotopomers could in principle have been formed, in which either H or D is involved in the intermolecular bond (PRZ ··· H′OD and PRZ ··· D′OH, where H′ and D′ refer to the hydrogen atoms involved in the hydrogen bond), but only the spectrum of the PRZ ··· D′OH species was observed. This could be due to the lower zero-point energy of the PRZ ··· D′OH complex, since the energy of the PRZ–D stretching vibration would, in a harmonic approximation, be $1/\sqrt{2}$ as great as that in a PRZ ··· H vibration.

The two component lines of each transition are interstate transitions between the two sublevels of the ground state, which arise from a low-energy motion on a double-minimum potential energy surface. In order to analyze simultaneously the 0^+ and 0^- levels we used a coupled Hamiltonian operator based on Pickett's reduced axes system (RAS) [Eq. (1)], and $\boldsymbol{H}(0^+)$ and $\boldsymbol{H}(0^-)$ are given by Equations (2) and (3).[22, 23]

$$\boldsymbol{H} = \boldsymbol{H}(0^+) + \boldsymbol{H}(0^-) \qquad (1)$$

$$\boldsymbol{H}(0^+) = \mathbf{H}_R(0^+) + \boldsymbol{H}_{CD}(0^+) \qquad (2)$$

$$\boldsymbol{H}(0^-) = \boldsymbol{H}_R(0^-) + \boldsymbol{H}_{CD}(0^-) + \Delta E \qquad (3)$$

$\boldsymbol{H}_R$ and $\boldsymbol{H}_{CD}$ are the rotational and centrifugal distortion Hamiltonian operators, and ΔE is the energy difference between the two states. Interaction terms of the type $F_{ab}(P_aP_b + P_bP_a)$, etc., provided by theory,[22, 23] were not taken into account here, as is usual for small ΔE values. The quartic centrifugal distortion parameters correspond to the irreducible representation $\mathbf{I}^r$ of Watson's "A" reduced Hamiltonian.[24]

Spectroscopic constants obtained with this approach are reported in Table 1. The centrifugal distortion parameters can be regarded as effective fitting parameters. For example, in a more detailed analysis the large values of the $\Delta_{J,K}$ and Δ_K parameters could be interpreted in terms of low-energy bending motions of the water molecule relative to the ring, while the opposite signs of the δ_K parameters for the 0^+ and 0^- states are probably due to non-exact interpretation of the two potential minima involved in internal rotational motions of the water molecule.

As shown above, the water molecule is linked to the lone pair of the nitrogen atom through one of the two protons. The quasi-zero values of the inertial defects (−0.23, −0.14, −0.37, and −0.52 u Å^2, for normal H_2O, $H_2{}^{18}O$, HDO, and D_2O species, respectively) suggest full planarity of the complex. This is supported also by the r_s substitution coordinates, obtained by application of Kraitchmann's equations[25] to average values of the rotational constants of the two sublevels of the four isotopomeric complexes. They are reported in Table 2 and provide further indications regarding the structure of the complex. The small non-zero values of $|b|$ and $|c|$ for the oxygen atom and the hydrogen atom involved in the hydrogen bond are probably due to the large amplitude motions underlying this type of molecular complex (see, for example, ref. [19]), and are therefore compatible with zero

Table 1. Rotational constants, centrifugal constants, and energy differences between the two sublevels of the ground state for the pyrazine/water complexes.

	Prz ··· HOH		Prz ··· H^{18}OH		Prz ··· DOH		Prz ··· DOD	
	0^+	0^-	0^+	0^-	0^+	0^-	0^+	0^-
A [MHz]	6290.15(3)	6290.20(3)	6288.90(3)	6289.00(3)	6279.79(4)	6279.72(3)	6251.12(3)	6251.01(3)
B [MHz]	1466.15(5)	1466.07(6)	1374.12(6)	1374.10(6)	1439.7(1)	1439.3(1)	1377.85(4)	1377.53(5)
C [MHz]	1190.43(6)	1188.82(6)	1128.58(6)	1127.48(5)	1172.7(1)	1170.96(9)	1130.80(5)	1129.77(5)
Δ_J [kHz]	2.42(6)	−1.08(8)	1.76(6)	−0.68(7)	2.8(1)	−1.9(1)	1.77(5)	−1.16(7)
Δ_{JK} [kHz]	7.4(5)	19.8(6)	7.7(4)	17.0(4)	4.4(8)	22.9(9)	7.5(4)	19.0(5)
Δ_K [kHz]	−9.1(6)	−14.8(6)	−7.3(6)	−10.2(6)	−5(1)	−18.9(9)	−5.8(6)	−13.4(5)
δ_J [kHz]	−1.09(6)	1.13(6)	−0.7(1)	1.2(1)	−1.7(3)	0.9(2)	−0.45(4)	1.02(4)
δ_K [kHz]	52(6)	−47(7)	56(6)	−29(6)	80(10)	−79(11)	38(5)	−76(6)
ΔE [MHz]	68.8(7)		51.6(5)		96.0(8)		67.8(5)	

Table 2. Substitution coordinates [Å] for the pyrazine/water complexes. The geometries of the complexed molecules correspond to those of the uncomplexed species (see text). The atom involved in the hydrogen bond is in each case indicated by a prime.

r_s Coordinates		$\|a\|$		$\|b\|$		$\|c\|$	
Complex	Atom	exp.	calcd. [a]	exp.	calcd.[a]	exp.	calcd.[a]
Prz⋯H′OH	O	3.432(3)	3.441	0.18(5)	0.07	0.16(6)	0.0
	H′	2.526(6)	2.559	0.25(5)	0.30	0.27(6)	0.0
	H	3.977[b]	4.021	0.56	0.69	0.29	0.0
Prz⋯D′OH	D′	2.501(6)	2.533	0.25(6)	0.29	0.26(6)	0.0
	H	3.952(4)	3.997	0.56(3)	0.66	0.29(6)	0.0

[a] Calculated with hydrogen bond parameters from the r_0 structure (see Figure 1 and text). [b] Obtained from the a coordinate of H in the Prz⋯D′OH complex by addition of the difference between the a coordinates of H′ in the Prz⋯HOH and the Prz⋯D′OH complexes.

equilibrium values. The larger $|b|$ value for the hydrogen atom not involved in the hydrogen bond indicates that this atom does not lie along the a axis, but always lies in the ab plane.

Alternatively, a plausible structure with the distance parameters for the vibrational ground state r_0 has been calculated from the rotational constants. The geometries of the two subunits have been taken from literature data on the isolated molecules water and PRZ,[21] except that for PRZ, for which an r_0 structure is not available, the C-N-C angle was changed from 115.6 to 116.7°. The hydrogen bond parameters are provided in Figure 1, and r_s coordinates calculated with this r_0 structure are compared to the experimental values in Table 2. The equilibrium configuration of the complex is shown in Figure 1.

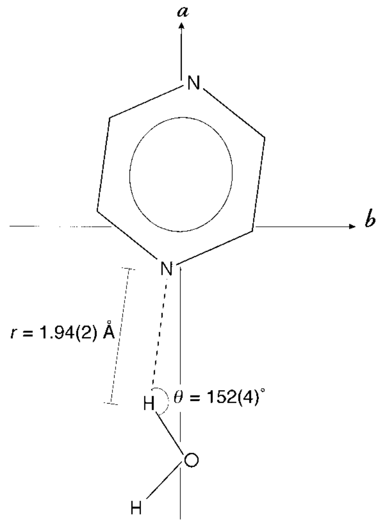

Figure 1. Geometry and principal axes system in the pyrazine/water complex.

The three translational and three rotational degrees of freedom of an isolated water molecule are replaced by six low-energy vibrational modes upon formation of the complex. One of these motions can be considered a stretching between the centers of mass of the two constituent molecules, while the remaining ones can be thought of as two bendings and three internal rotations of the complexed water moiety. Considering the equivalent configurations generated by these motions, and the fact that the water molecule can be bound to either of the two ring nitrogen atoms, the potential energy surface that describes the position of the water molecule with respect to the PRZ molecule is characterized by eight equivalent minima. Only one of the barriers connecting these minima can determine the vibrational spacings (ΔE) reported in Table 1 and is low enough to produce the doubling we have observed for all transitions. This motion can be interpreted as an internal rotation of the water molecule along the H–N bond relative to the ring. Going from one of the two equivalent minima to the other (see Figure 2) inverts the μ_b component of the dipole moment, which implies that each μ_b-type transition takes place across the two vibrational sublevels. Furthermore, and in agreement with the permutation group theory of non-rigid molecules,[26, 27] the ratio of intensities of these transitions is established by the two pairs of equivalent hydrogen atoms on the ring; that is, 5:3 for rotational levels of the ground state (0^+) for even K_a, and 3:5 for odd K_a. The reverse is true for the 0^- state.

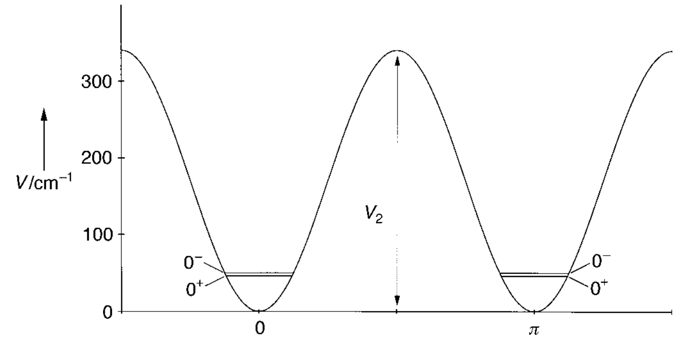

Figure 2. Potential energy function V for internal rotation of the water molecule with respect to the pyrazine ring.

A quantitative description of this torsion has been obtained by application of Meyer's one-dimensional flexible model[28] to the ΔE splittings of the four isotopic species, with the V_2 parameter determined according to Equation (4), where τ is the internal rotational angle of the water molecule (coinciding with the O-H-N-C dihedral angle).

$$V(\tau) = 1/2\, V_2(1 - \cos 2\tau) \qquad (4)$$

The value of the N-H′-O angle also proved to be an important model parameter, related to the kinetic part of the motion, and it was determined to be about 140°, not very different from the value for the r_0 structure presented in Figure 1. The range 2π for τ has been resolved for the calculation into 21 mesh points.[28] The results of the calculations are shown in Table 3. Two different values of V_2 have

Table 3. Experimental values and energy differences obtained from the flexible model for internal rotation of the water molecule relative to the pyrazine ring in the four isotopomeric pyrazine/water complexes.

	Prz···HOH[a]	Prz···$H^{18}OH$[a]	Prz···DOH[b]	Prz···DOD[b]
$\Delta E_{exp.}$ [MHz]	68.8(7)	51.6(5)	96.0(8)	67.8(5)
$\Delta E_{calcd.}$ [MHz]	68.2	52.1	97.8	64.3

[a] Parameters utilized: $V_2 = 346\ \text{cm}^{-1}$, $\theta = 140°$. [b] Parameters utilized: $V_2 = 308\ \text{cm}^{-1}$, $\theta = 140°$.

been fitted, depending on the isotopic species of hydrogen (H′ or D′) involved in the hydrogen bond. A lowering in the V_2 value by about 10% occurs upon introduction of a deuterium atom into the hydrogen bond. This is probably related to the Ubbelohde effect:[29] that is, a shrinkage of the hydrogen bond upon deuteration, which also reduces the distances between the participating heavier atoms of the two subunits.

The two remaining torsional motions of the water subunit would imply rupture of the hydrogen bond, with a correspondingly higher barrier to internal rotation. As a consequence, we did not observe further splittings of the rotational lines due to these motions.

The effects of the two bending motions are reflected in the anomalously high values of the centrifugal distortion parameters Δ_{JK} and Δ_K, as described for several complexes of aromatic molecules with rare gases.[9–20]. Information regarding the force constants for these motions can be obtained in a rather straightforward way from the rotational spectrum when the complex is a symmetric top.[9] It can also be obtained through a more complicated procedure for molecular complexes with C_s symmetry,[30] but this task appears to be difficult in our particular case.

A comparison of our results on PRZ···H_2O with those obtained for the benzene/water complex[2, 3] shows that completely different hydrogen bonds characterize the two complexes. We believe that the type of interaction we have studied is one of the most common in nature, and that our results can therefore serve as a firm experimental starting model for the interpretation of similar linkages in more complicated natural systems.

Experimental Section

The Stark and pulse-modulated free jet absorption millimeter-wave spectrometer used in this study has already been described elsewhere.[18] Complexes were formed in a stream of argon saturated with water at room temperature and a pressure of about 2 bar that passed over samples of PRZ heated to about 40 °C. The mixture, at a stagnation pressure of 0.5 bar, was expanded to about 5×10^{-3} mbar through a pulsed nozzle (repetition rate 5 Hz) with a diameter of 0.35 mm, which produced an estimated "rotational" temperature of about 10 K. All samples involved commercial materials utilized without further purification. The accuracy of the frequency measurements is about 0.05 MHz.

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